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DIETHANOLAMINE AS CO_2 ABSORBENT FOR ^{14}C ANALYSIS TO DETERMINATION AGE OF CORAL REEF FROM PANAMBUNGAN ISLAND BY USING *LIQUID SCINTILLATION COUNTING* (LSC) METHOD

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ABSTRACT

Utilization of diethanolamine (DEA) as an absorbent for ^{14}C analysis using liquid scintillation counting (LSC) on the determination of the age of the coral reefs have been done. Coral reefs are analyzed from the uninhabited Panambungan island which far away from the influence of human activity. Sample preparation, physical and chemical by using 2 acid-base mixture: H_2O_2-NaOH and $HClO_4$-HCl. At this stage there is a weight reduction of as much as 9.023 gram sample. Carbonate samples reacted with HCl to separate CO_2 and sequestration by diethanolamine into carbamate compounds. Total carbon in the sample solution is obtained through the reduction of 0.838 grams before and after absorption. The specific activity of ^{14}C in samples measured by the counter LSC HIDEX 300 SL and obtained 8.4026 ± 6,85 DPM/gC. The specific activity of the sample and the specific activity of modern carbon (15.3 ± 0.1 DPM/gC) is inserted into the equation radioisotope decay, obtained the age of 4955 ± 935 years.

Keywords :Dietanolamine, Liquid Scintillation Counting, Coral, Panambungan Island

1. INTRODUCTION

Marine and coastal Indonesia has been known for it's wealth and biological diversity (biodiversity) in the world, with a coastline of 81,000 km and the sea area of about 3.1 billion km^2. Approximately 18% of the world's reefs are in Indonesia waters[6][4].

One of the areas in Indonesia which has a wide range of diversity of marine life, namely South Celebes province. The province has many islands such as Sembilan Archipelago in the Gulf of Bone, Taka Bonerate Archipelago in the Flores Sea, and Spermonde Archipelago in the Makassar Strait. Spermonde Archipelago is a region with the deployment of the reef is quite wide, the number of islands around 120 islands[15]. Coral species live in Spermonde Archipelago totaled 250 species of coral reefs in the area of 150 km^2[3]. Diversity of coral species can be found on the Panambungan island located in Pangkep with an area of 100 m^2 and coral reef condition is quite good[19].

Coral reefs are the oldest ecosystems that are economically and biologically important in the world [13]. Massive coral reefs composed of precipitated calcium carbonate ($CaCO_3$) which can be grown on the scale of millimeters to centimeters annually. During the growth process will form the framework (skeleton) of coral reefs and the annual cycle (annual band) that can be used for the chronology of the formation of coral reefs. During the process of formation of coral skeletons also occurs incorporation of isotopes and elements that reflect the environmental conditions in the surrounding sea, such as sea surface temperature, hydrological equilibrium (evaporation and precipitation) and ocean circulation[1].

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Coral reefs contain radioactive elements measured isotopes of carbon, namely carbon-14 (^{14}C). ^{14}C element emits beta particles (β) and will disintegrate in the period 5730 half year to ^{14}N are stable[5]. Carbon-14 survive in materials such as trees and rocks that have been aged tens of thousands years. This is useful for radiocarbon dating[20].

Methods used radiocarbon dating to determine the age of objects. The measurement is based on the calculation results of activity of ^{14}C or ^{14}C ratio of the amount of radioactive isotopes that exist on the object using a standard known quantity radioactive isotopes[18].

Beta (β) energy from ^{14}C emittedis very low, as well as the specific activity of the resulting samples. Therefore, for the enumeration of radiation emitted by the ^{14}C required a special counter to the very low background radiation (Low background Counter), to obtain high accuracy in interpreting the data of the count. Counting that can be used is Liquid Scintillation Counting (LSC)[24].

Liquid Scintilation Counting is popularly used for radiocarbon dating, which tend to be very good for a sample of the organic solvent or in solid form, conveniently in sample preparation, data processing, and the ability of the spectrometer to analyze different nuclides simultaneously, geometrically measurement counting can achieve efficiencies around 99.99 %[22;2].

There are two methods in the analysis of radiocarbon sample pretreatment with LSC, namely benzene synthesis and CO_2 absorption[23].This absorption methods more easily than other methods, since it is much more economical and simple[17]. To absorb CO_2, use a solution that has the ability as absorbent.

The used Diethanolamine (DEA) as absorbent CO_2 absorption results obtained the highest CO_2 than the other two compounds alkanolamine, with power absorption of 0.658 mol CO_2/mol amine [11]. DEA highest absorption efficiency as much as 59.08% of the samples of coral reefs [14]. Based on DEA compounds ability to absorb CO^2, the compound will be used as absorbents for determining the age of the coral reefs in this research.

2. METHODS

Time and Location

The study was conducted in May through August 2016 Radiation Chemistry Laboratory Chemistry Department, Faculty of Mathematics and Natural Sciences Hasanuddin University.

Tools and Materials

Tools

The tools are used: glass tools commonly used in the laboratory, Erlenmeyer, glass beaker, petri dish, pumpkin spray, burette, pipette scale, pipette volume, pipette, flask, beakers, bulb, stirrer, hotplate, suite of tools absorption, impinger, LSC count tool Hidex 300 SL, vial scintillator, Ruler, stative, mortal, gloves, baskets, oven and hammer

Materials

The materials used are HCl 10 %, NaOH 1 N, $HClO_4$ 1 N, KOH 0,1 N, H_2O_2 30%, $AgNO_3$, silica gel, N_2gas,coral reefs, marble as background material, Aqualight scintillator, filter paper, aluminum foil, tissue and distilled water.

Sampling

Sampling is done in the Panambungan island, District Tupabiring, Pangkep, South Celebes with capture

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location at coordinates S : 4º5719,552", 119º21'54,84" with a depth of 4-5 meters above sea level. Sampling coral reefs of the locations aided by divers using a stingy, drill and hammer. Pieces of coral sample is placed into the sample nets and brought to the surface to be placed in a box cooled to below to the laboratory.

Cleaning Sample

Cleaning aims to eliminate impurities in the samples of coral reefs. Cleaning is done in two stages, the physical leaching and chemical leaching. Where in physical washing sample with running water while brushed and rinsed with distilled water several times, then performed the leaching of chemicals to eliminate the source of the carbon surface, organic stains and several matrices dissolved accumulated in the samples of coral reefs over the waters by immersing a sample in a mixture of H_2O_2 30% and 1 N NaOH 50:50 in a beaker of 100 mL while diultrasonik for ± 10 minutes. After the sample is washed and rinsed, soaked samples back in the mix (1: 1) 30% H2O2 and 1 N $HClO_4$ for ± 30 seconds and the last process in the chemical leaching is a sample immersed in 6 N HCl, rinsed with distilled water.

Separation of Carbamate Sample

Carbonate coral reefs separated as CO_2 by adding HCl10% in the 10 g sample and to form gas bubbles and carbonate samples completely reacted with HCl 10% (Figure 1). Bubbles of gas produced is passed into the water absorbent ($AgNO_3$), acid absorbent (silica gel) and passing absorbent solution (DEA) to produce a carbamate dissolved by the reaction as follows:

$$CO_2 + 2\ R_2NH \rightarrow R_2NCOO^- + R_2NH_2^+$$

(R = $-CH_2-CH_2-OH$)

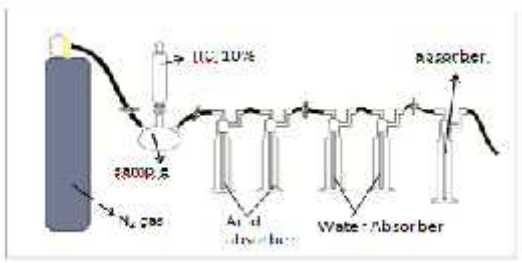

Figure 1 Design tools as CO_2 separation carbonate reef sample

Sample Enumeration

Sample enumeration is done by filling in 8 mL of sample solution (dissolved carbamates) and 12 mL scintillator into a 20 mL vial. Homogeneous mixture of sample and scintillator enumerated with the LSC Hidex 300 SL with a time pencacahan1-240 minutes. Enumeration generate data in units of counts CPM (Counts Per Minute), TDCR (Triple To Double Coincidance Ratio) and DPM (decays Per Minute) obtained from the CPM with TDCR samples.

Determined of Age

Age sample coral reefs can be calculated based on the ratio of the specific activity of modern carbon (15,3 ± 0.1 DPM/gC) to a specific activity of sample obtained from the enumeration by using radiocarbon decay rate equation :

$$t = \frac{t_{1/2}}{\ln 2} \ln \frac{A_0}{A}$$

A = Radioactivity of 14C isotopes in the sample

Ao = Radioactivity isotope ^{14}C during the life of plants or animals (15.3 ± 0.1DPM)

$t_{1/2}$ = Half-life ^{14}C = 5730 ± 40 tahun

ln2 = 0.693

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3. RESULTS AND DISCUSSION

Samples obtained coral reefs in PanambunganIsland located in Pangkep, precisely in the Village Mattiro Sompe, District Liukang Tupabiring. Selection of sampling sites due Panambunganisland is uninhabited, so that the authenticity biota waters are protected from human activity and also the condition of coral reefs around the island in general is still very good.

Results Cleaning Samples Coral Reef

Washing the sample conducted two stages, physically and chemically leaching able to eliminate all natural contaminants found in samples of coral reefs, thus resulting corals appear white due to the loss of impurities and carbon source on the sample surface. It is known by way of the weighing of dry samples of coral reefs to obtain permanent weight to the value of 24.542 grams and sample weight loss of 26% of impurities. Where the sample is missing a natural contamination accumulated over the reef in the waters as well as the matrix of the rock face dissolved.

Sample Enumeration Results

Liquid Scintilation Counter (LSC) HIDEX 300 SL provides activity data ^{14}C in the sample based on the emission of a negative beta particle (β) which decay to reach a steady state by emitting electrons. Measurable results in the form of chopped tool per minute (CPM), desintegration per minute (DPM) and triple to double coincidence ratio (TDCR).

The results obtained from the sample enumerated from minutes to 5-180, showed fluctuations count values. CPM impairment occurs because the number of nuclei decay during certain time intervals decreased exponentially. The decline in the value of CPM a sample proportional to the decline in value of DPM but inversely proportional to the value TDCR. In the 90 minute the value of ^{14}C activity began to achieve stability, it is shown by the CPM and DPM stable. CPM values obtained amounted to 60.010, DPM amounted to 102, 500 and TDCR value of 0.584. Fluctuations in the enumeration Increased count values at 180 minutes due to the effects of the instability of the phase between the sample solution with the dissolved CO_2 DEA-scintillator. Phase stability also affects the efficiency of enumeration (TDCR), with the highest ^{14}C counting efficiency of about 80% or 0.8 [8], TDCR value that indicates the efficiency of the enumeration in the minutes to 90 minutes higher than 60 and 120. The same treatment is done against a background enumeration to obtain the optimum time. Scintillator solution of 12 mL vial was added and the resulting solution was added 8 mL DEA absorption and marble as backgound. Marble chosen as the background for a material that is considered not leave a radioactive activity or activities close to zero. So it is used as a correction factor to the atmospheric cosmic rays as measured by LSC [14]. Count values of 5-90 minutes to the relatively decreased and increased after passing minutes to 90. The optimum time in the census enumeration background ie the 90th minute with a value of 57.030 CPM, DPM at 99.440 and TDCR at 0.573. When compared to the value of the sample DPM, DPM has a marble background using DPM lower value, so that the enumeration of data can be used to correct the count of 14C activity in the samples. Data chopped optimum time of the sample and the background can be seen in Table 1.

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Table1 Results of Enumeration Data Timing Samples Optimum Coral Reef and Background

Sampel				***Background***		
Waktu cacahan (menit)	**CPMs**	**DPMs**	**TDCRs**	**CPMb**	**DPMb**	**TDCRb**
5	56,800	107,540	0,528	64,400	115,200	0,559
15	63,800	108,830	0,586	62,330	109,760	0,567
30	60,100	103,000	0,583	60,060	102,590	0,585
60	60,010	103,750	0,578	59,130	102.990	0,524
90	60,010	102,500	0,585	57,030	99,440	0,573
120	59,710	102,250	0,584	57,250	97,930	0,584
150	57,600	97,920	0,588	57,180	98,060	0,583
180	58,100	98,800	0,588	57,360	100,710	0,569

Chart comparison of CPM and DPM sample and the background with time can be seen in Figure 2 below:

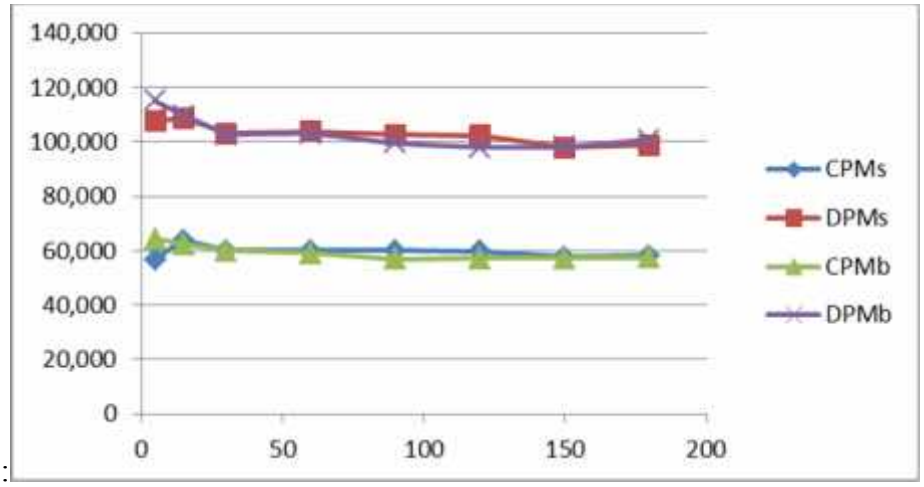

Figure 2: Comparison of CPM and DPM samples against time

The optimum time obtained is used to determine the value of the average activity of ^{14}C in samples of coral reefs and background with five repetitions. Furthermore, the average value is used to obtain a specific activity in the samples of coral reefs. Results enumeration repetition as much as 5 times the CPM values obtained by an average of 58.836, an average value of DPM 100.970, and TDCR average of 0.5802. Background chopped results obtained with the average value of CPM, DPM and TDCR amounted to 58, 392, 100.586, 0.5786. The average yield on the enumeration background is used to get the value of disintegrations per minute (DPM) ^{14}C in the sample based on the difference of the value of the sample DPM and DPM background. The use of the results of the enumeration background as a correction factor that gives information about the amount of radiation that is not derived from a sample rather than the environment LSC itself. Data from the

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repetition of a sample census of coral reefs and the background can be seen in table 2:

Table 2. Enumeration Sample Results Data Coral Reef and Background with five repetitions

Waktu Cacahan (menit)	CPMs	CPMb	DPMs	DPMb	TDCRs	TDCRb
90	58,820	57,420	101,270	100,420	0,580	0,571
90	59,490	60,600	101,270	101,220	0,587	0,592
90	58,910	58,230	101,510	101,330	0,579	0,574
90	58,230	59,170	100,820	100,500	0,577	0,588
90	58,730	56,540	99,980	99,460	0,587	0,568
Rata-rata	58,836	58,392	100,970	100,586	0,5802	0,5786

Determination of the Activity Sample

The specific activity (As) samples of coral reefs form the basis for age determination. The specific activity obtained from the difference in count values of disintegration per minute (DPM) samples and disintegration per minute (DPM) background divided by the total carbon in 8 mL sample. specific activity calculation results can be seen in Table 3.

Table 3 Specific Activity data The average ^{14}C Sample Panambungan Islands Coral Reef Spermonde Archipelago

Coral Reef	DPM	C-total (g)	As(DPM/gC)
	0,384	0,457	8,4026 ± 6,85

According to the table above, obtained specific activity of ^{14}C in the sample 8.4026 ± 6.85 DPM/gC. Values obtained specific activity lower the value of the average activity of ^{14}C in the atmosphere in the range of 15.3 ± 0.1. It shows there has been a decay in carbon nuclei in the sample when the sample shows no life activity. The specific value average ^{14}C obtained showed disintegration number of carbon atoms which decays per minute (DPM) in one gram unsure per gram of carbon.

Determination Age of Sample

Age samples of coral reefs is determined by comparing the 14C radioactivity of living beings who are still alive as Ao and ^{14}C radioactivity in the samples as At formulated as follows [10];

$$t = \frac{t_{1/2}}{\ln 2} \ln \frac{A_0}{A}$$

A = Radioactivity of 14C isotopes in the sample

Ao = Radioactivity isotope ^{14}C during the life of plants or animals (15.3 ± 0.1DPM)

$t_{1/2}$ = Half-life ^{14}C = 5730 ± 40 tahun

ln2 = 0.693

based on the equation above, the age of the samples of coral reefs Panambungan Island Spermonde Archipelago can be seen in Table 4.

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Tabel 4 Data Calculation Results Age Panambungan Islands Coral Reef Spermonde Archipelago

SampleAge (years)	
Coral reef	4955± 935

The results of the determination of the age of the coral reefs by the method of liquid scintillation counting (LSC) by measuring the radioactivity of ^{14}C provides the results of 4955 years of age. When compared with the age of the previous studies that found much different age, where age Langkai Island and LanjukangIsland in the Spermonde Archipelago give the age range between 400-600 years[14].

4. CONCLUSION

Age reef origin Panambungan Island in the Spermonde Archipelagowere calculated based on the specific activity of carbon-14 is 4955 years old.

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